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含铁多相催化剂催化的丙烯环氧化

Epoxidation of Propylene Catalyzed by Iron-Containing Heterogeneous Catalysts

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摘　要

本论文合成了含铁分子筛，考察了分子筛中不同位置的铁物种在丙烯环氧化反应中的催化反应性能差异，并对催化剂结构进行了详细的表征，进而深入探讨了催化剂结构和性能之间的关联。

首先，利用直接水热合成法，模板剂离子交换法和浸渍法合成了铁处于分子筛中不同位置的Fe-MCM-41 催化剂，并向其中添加钾盐进行修饰。研究发现，添加KCl后，不同方法合成的Fe-MCM-41 均能够实现丙烯氧化由烯丙基氧化向环氧化的转变。多种表征手段结果表明，添加KCl会导致骨架外铁物种由扭曲的八面体结构向为K^+离子所稳定的正四面体结构转变，该正四面体结构的铁物种是丙烯环氧化的活性位。对于骨架内四配位的铁物种来说，加入KCl会引起骨架铁物种的脱出，而引起分子筛结构的破坏，但脱出骨架的铁物种由于受到骨架的影响，难以与K^+形成正四面体构型。铁配位结构上的差别导致了其在丙烯气相环氧化中反应性能的不同。对不同阴离子钾盐的考察发现，添加KCl的催化剂具有最好的催化性能。

本论文合成了 ferrisilicate 催化剂，对其进行水蒸汽处理，随后以 KCl 进行修饰，同时以未经水蒸汽处理的催化剂添加 KCl 作为对比，研究其在丙烯环氧化反应中的性能。催化性能结果表明，水蒸汽处理后，添加 KCl 的催化剂在 ferrisilicate 系列催化剂中表现出了最好的催化性能。各种表征结果表明，ferrisilicate 中的铁物种与骨架结合紧密，仅添加 KCl，难以将铁脱出骨架并形成有效的活性位，经水蒸汽处理后，则能成为表面铁物种，在 KCl 的作用下可以形成有利于丙烯进行环氧化反应的正四面体配位结构的新铁物种。

通过对 Fe-MCM-41 和 ferrisilicate 的研究发现，催化剂中添加 KCl 不仅可以使铁物种形成有利于丙烯环氧化反应的正四面体结构，还可以使铁的可还原性能显著降低，从而抑制晶格氧的活性，进而抑制了烯丙基氧化。

关键词：丙烯环氧化；含铁分子筛；KCl 修饰；水蒸汽处理

Abstract

In this dissertation, KCl modified molecular sieves that contain iron species in- or extra-framework are synthesized to study their different catalytic performances for propylene epoxidation with N_2O. These catalysts have been characterized in details and the structure-reactivity relationships have also been investigated.

Fe-MCM-41 catalysts are synthesized and iron would be introduced into different positions of MCM-41by direct hydrothermal synthesis (DHT), template-ion exchange (TIE) and impregnation (IMP) methods. It is found that the main reaction route can be shift from the allylic oxidation to the epoxidation over Fe-MCM-41 catalysts with modification by KCl. The characterizations by XRD, N_2-adsorption, Raman, UV-Vis and H_2-TPR indicate that after the modification, the coordination structure of ex-frame iron species is probably changed from distorted octahedron to tetrahedron stabilized by potassium ions. The tetrahedrally coordinated iron sites are proposed to be the active sites for the propylene epoxidation. As to the in-frame iron species, they are impelled to migrate into extra-framework positions during the KCl modifying process, which cause the collapse of mesopores. The migrated iron species hardly form tetrahedral conformation with potassium ions because of the impact of framework, which results in the low propylene conversion over KCl-Fe-MCM-41-DHT catalysts. The effect of other potassium salts has been studied. It is found that the catalyst modified by KCl exhibits the best catalytic performances for propylene epoxidation.

A series of different ferrisilicate catalysts are steam-activated and then modified by KCl. Meanwhile, ferrisilicate that are not steam-activated but modified by KCl are used as comparisons to illuminate the effect of different-positioned iron species on propylene epoxidation. Catalysts that are steam-activated and then modified by KCl exhibit superior catalytic performances. The detailed characterizations indicate that in-frame iron species cannot form effective active sites for epoxidation without steam-activated. Steam-activation is required to massively create extra-framework iron species. The coordination structure of resulted extra-framework iron species is changed to tetrahedral coordination that favors epoxidation of propylene. KCl-s-ferrisilicate (Si/Fe=64, K/Fe=2, steam-activated time: 8h) catalyst shows the best catalytic performance.

The studies also found that KCl played the important roles. First, the reducibility of iron species became difficult, indicating the reactivity of lattice oxygen was inhabited and the allylic oxidation was also suppressed. The second is that iron tetrahedral coordination structure was formed and stabilized by KCl, which contribute to epoxidation of propylene.

Keywords: Propylene epoxidation, iron-containing molecular sieves, KCl modification, steam-activation

第一章 绪　论

1.1 催化与选择氧化反应

选择氧化反应在自然界和人类社会占据着重要的地位。催化剂参与了大部分选择氧化反应，如与生命体活动紧密相关的酶催化反应。催化选择氧化是化学品工业生产的重要组成部分。在以催化生产的化学产品中氧化产物占有很高比例。以烷烃类为原料的选择氧化因其资源丰富、价格便宜、产物附加值高等原因，而成为了催化研究的热点研究领域。

Table 1-1 Industrial process for oxidation of hydrocarbons developed during the past 4 decades[1]

Process	Phase	Catalyst
Naphthalene to phthalic anhydride	Gas	V-K-O
Ethylene to acetaldehyde	Liquid	Pd-Cu-Cl
p-Xylene to terephthalic acid	Liquid	Cu-Mo-Cl
Butene to maleic anhydride	Gas	V-P-O
Methanol to formaldehyde	Gas	Fe-Mo-O
Propylene ammoxidation to acrylonitrile	Gas	Complex oxide
Propylene to acrolein	Gas	Complex oxide
Acrolein to acrylic acid	Gas	V-Mo-O
Ethylene & acetic acid to vinyl aceteate	Liquid	Pd-Cu-Cl
o-Xylene to phthalic anhydride	Gas	V-Ti-O
Propylene to propylene oxide	Liquid	Ti-Mo-O
Butanol to methylcrilate	Liquid	MoO3
Ethylene to vinyl chloride	Gas	Cu chloride
Butane to maleic anhydride	Gas	V-P-O
Phenol to hydroquinone & catechol	Liquid	TS-1

表 1-1 是近年来应用在烃类选择氧化工业中的反应[1]，这些反应已经成为整个现代化学工业的一个重要支柱。虽然研究人员在烃类选择氧化方面